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Magnetic field induced metal-insulator transition in colossal magnetoresistive $Pr_{1-x}Ca_xMnO_3$ (x = 0.0–0.7) material

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Abstract . In zero field $Pr_{1-x}Ca_xMnO_3$ shows thermally activated behaviour for all values of x. For $x \geq 0.3$, charge ordering occurs at 250 K, with long range antiferromagnetic ordering at lower temperature. For a range of compositions $0.3 \leq x \leq 0.45$, a first-order magnetic-field-induced insulator-metal transition produces changes in resistivity of up to 12 order of magnitude at low temperature. These conducting states are metastable, resulting in a large hysteresis in resistivity with changes in both magnetic field and temperature

Keywords . Magnetoresistance, perovskite manganates, insulator-metal transition

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1. Introduction

Large negative magnetoresistance (MR) is of current interest due to the possibility of producing devices which making use of this effect. The substitution of divalent ions on the rare-earth (R) site in $RMnO_3$ compounds, yield materials for which the application of a magnetic field produces very large decreases in resistivity [1-5]. The application of a magnetic field can also increase the temperature at which long-range ferromagnetic order is observed. As a result, these materials can be driven between a low- and high conductivity state by application of a magnetic field. Perovskite structured lanthanum manganite ($LaMnO_3$) can be made to exhibit both strong ferromagnetism and metallic conductivity by partial substitution of La ions (3+ valence) with 2+ valence ions such as Ca, Ba, Sr. This results in a Mn^{3+}/Mn^{4+} mixed valence state creating mobile charge carriers and canting of Mn spins [6,7]. The magnetoresistance had observed in polycrystalline, thin films and single crystals [8-10]. The MR ratio is defined as $\Delta\rho / \rho_0 = (\rho_H - \rho_0) / \rho_0$.

This behaviour is usually explained in terms of the double exchange theory [11-13]. Doping produces a decrease in the Mn^{3+} / Mn^{4+} ratio making it easier for electrons to hop between Mn ions and creating a tendency for ferromagnetic interactions rather than the antiferromagnetic exchange interactions which dominate if the electrons are more localized.

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In zero magnetic field, $Pr_{0.7}Ca_{0.3}MnO_3$ exhibits three phase transition : a change of the lattice symmetry at T_B = 200K, an antiferromagnetic ordering at T_N = 140K and a canted antiferromagnetism at T_{CA} = 110K. Although the resistivity of $Pr_{0.7}Ca_{0.3}MnO_3$ shows insulating behaviour at zero field. It exhibits an insulator- metal transition at around 4T at 5K. An applied field enforces a ferromagnetic spin alignment and drives $Pr_{0.7}Ca_{0.3}MnO_3$ into the metallic state by actuating the double-exchange mechanism and destroying the charge ordering.

2. Experimental details

Samples of $Pr_{1-x}Ca_xMnO_3$ ($0 \leq x \leq 0.7$) were prepared by a solid state reaction method from the high-purity reagents Pr_6O_{11}, $CaCO_3$ and MnO_2. The starting materials were mixed in stoichiometric proportions, ground and sintered at 1300°C for 12 hours. The resulting powders were reground, sintered at 1350°C for 12 hours in air and cooled to room temperature in the furnace. The powders were pressed into pellets and sintered at 1350°C for 24 hours.

The prepared materials were characterized by X-ray diffraction. Measurements of the resistivity as functions of magnetic fields of upto 8T and temperature of upto 4 K, were carried out using a standard dc four -probe method. An excitation current of between 1 to 1000 μA was used, depending on the resistance of the sample.

3. Results and discussion

The X-ray spectra obtained showed all samples to be nominally single phase. Figure 1 contains curves showing the variation in the resistivity as a function of temperature for several samples with different Ca concentrations. In zero field the magnitude of the resistivity at 273 K decreases from around 800 Ω cm for $x = 0.0$ to 0.003 Ω cm at $x = 0.7$ (see Figure 2).

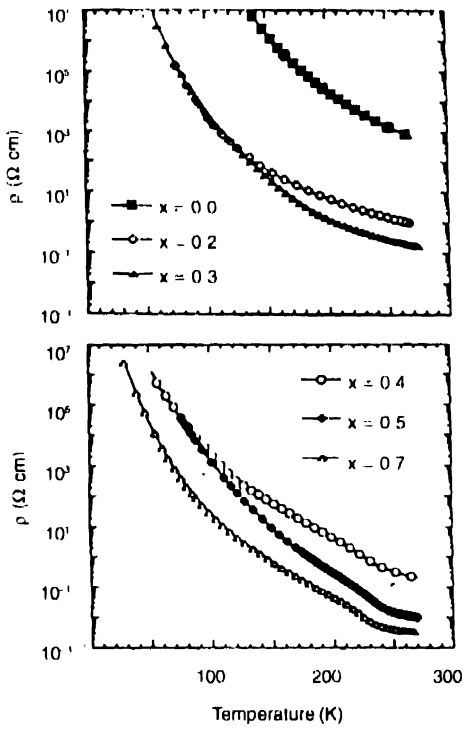

Figure 1. Resistivity *versus* temperature data collected in zero field for several $Pr_{1-x}Ca_xMnO_3$ samples. For $0.2 \leq x \leq 0.7$ a distinct change in slope around 250 K indicates the onset of charge ordering.

For all values of x, the resistivity and $-d\rho/dT$ increase with decreasing temperature. We have fitted the $\rho - T$ data for the whole composition range studied using a simple exponential expression of the form $\rho = \rho_0 \exp(T_0/T)^p$, where T_0 is some effective temperature and p is a positive exponent. We have calculated values for the activation energy using $p = 1$. For $x \leq 0.2$, a fit produces a single value for the activation energy over the entire temperature range examined. For higher values of x, there is a distinct change in slope of $\rho - T$ at around 250 K associated with a structural transition and possibly charge ordering. This leads to an increase in the activation energy below this temperature for each composition. The activation energy at high temperature decreases with increasing x across the series from 0.2 eV at $x = 0.0$ to 0.03 eV at 0.7 (see Figure 2).

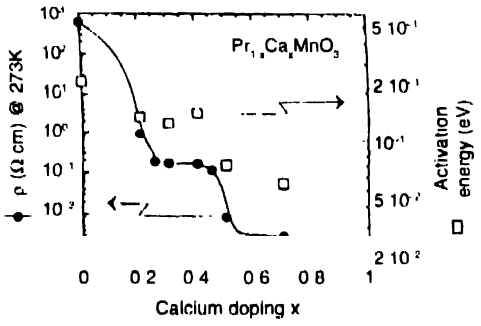

Figure 2. The variation in the zero field resistivity at 273 K and the activation energy as a function of calcium for doping for the $Pr_{1-x}Ca_xMnO_3$ series.

In a field of 8 T, the resistivity initially increases with decreasing temperature for all of the samples studied (see Figure 3). For each composition, the magnitude of the resistivity at 273 K and 8 T is lower than the zero- field value. This reduction corresponds to a negative MR, $\Delta\rho/\rho 0$, where

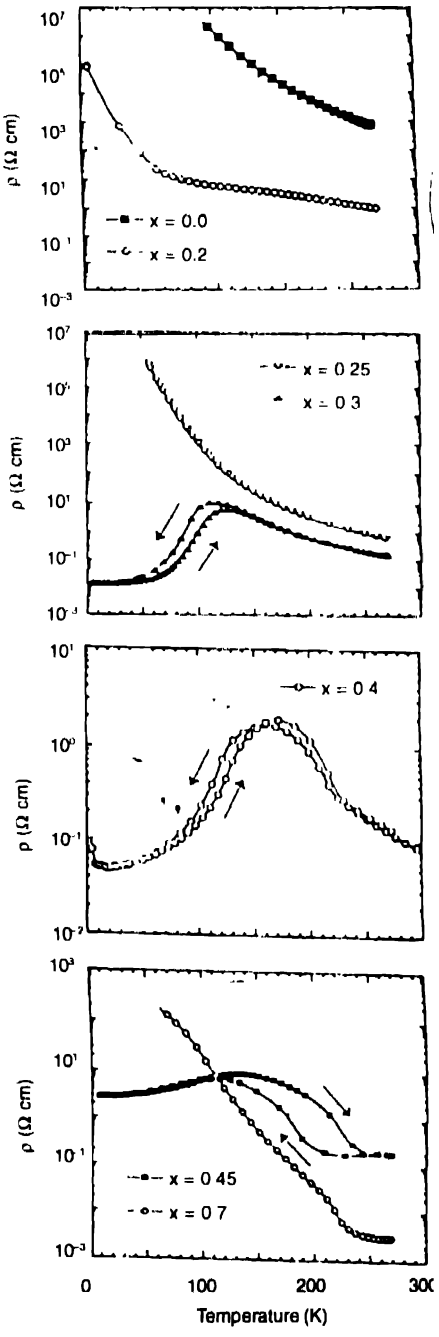

Figure 3. Resistivity *versus* temperature data collected in a magnet field of 8 T for several $Pr_{1-x}Ca_xMnO_3$ samples.

$\Delta\rho = (\rho H - \rho 0)$, of around 3% over a wide composition range. For $0.5 \leq x \leq 0.7$ a clear feature indicating the onset of charge ordering and a structural transition is present at around 240 K. For a more limited composition range $0.3 \leq x \leq 0.45$, the resistivity for 8 T has a peak at around 150 K and then falls in some cases by several orders of magnitude. The magnitude of the resistivity observed below 10 K yields negative MR values in excess of 99.999%.

Temperature-cycling experiments, in various applied magnetic fields, have been performed on several samples. The results for the $x = 0.3$ composition are shown in Figure 4. This sample exhibits activated behaviour in applied fields of less than 3 T although the magnitude of the resistivity decreases slightly with field. In higher fields, a peak appears in the resistivity *versus* temperature data which is followed by a rapid fall in resistivity at lower temperatures. As the applied magnetic field is increased, the position of this peak is shifted to higher temperature and the magnitude of the resistivity falls. At 4 K, the value of the resistivity can be varied by at least 12 orders of magnitude depending on the value of the applied field. On warming from low temperature in fields greater than 4 T, there is a further decrease in $\rho - T$ producing a minimum at around 40 K. The difference between cooling and warming curves shows hysteresis in the data with a width of up to 100 K. Similar results have been obtained for samples with $0.3 \leq x \leq 0.45$.

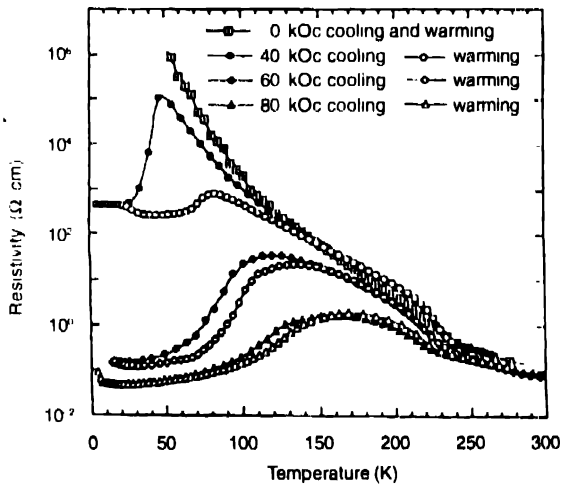

Figure 4. Resistivity *versus* temperature curves for $Pr_{0.7}Ca_{0.3}MnO_3$ taken in several magnetic field

Figure 5 shows the resistivity *versus* magnetic field at fixed temperature for the same $x = 0.3$ sample. For each loop, the sample was first zero-field cooled from room temperature to the measuring temperature. At 4 K, the resistivity is initially above the limit which we can measure. As the magnetic field is increased, there is a rapid fall in $\rho - H$ around 5 T. The resistivity falls by more than seven orders of magnitude within 5 T. A more gradual decrease in $\rho - H$ by a further two orders of magnitude is observed upto 8 T. Sweeping the field back to 0 T, produces only a small increase in the magnitude of the resistivity. Around 50 K, there is a more gradual appearance of a high-conductivity state for fields of around 4 T. At temperature of upto 130 K, the resistivity falls with increasing magnetic field corresponding to a negative MR of 99.9%. There are no discontinuities in the data and the $\rho - H$ loops open up only for higher fields. At higher temperature, a negative MR still exists but the behaviour is essentially reversible over the entire field range studied and the changes in the value of $\rho - H$ are much smaller in magnitude. Similar magnetic -field- induced transitions to a state with low resistivity at low temperature, have been observed in samples with $0.3 \leq x \leq 0.45$ The field -induced conducting state observed at low temperature for $0.3 \leq x \leq 0.45$ are metastable.

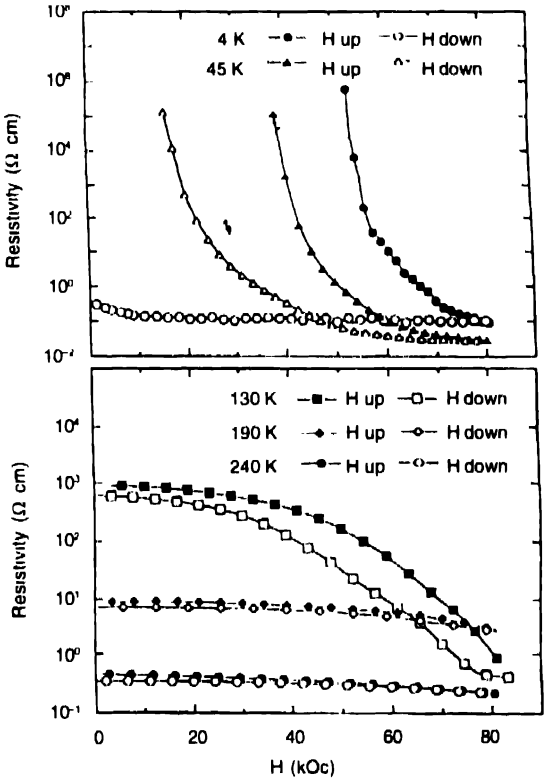

Figure 5. Resistivity *versus* magnetic field curves for $Pr_{0.7}Ca_{0.3}MnO_3$ taken at several temperatures.

4. Summary

Magnetic field – induced insulator – metal transitions are shown to occur for the range of Ca compositions $0.30 \leq x \leq 0.45$. Within this composition range, the dramatic changes in the resistivity are accompanied by regions of hysteresis extending over a considerable range of temperature and magnetic field. The high conductivity states are shown to metastable at low temperature. We also show that for $Pr_{0.7}Ca_{0.3}MnO_3$ compounds, there is a clear correlation between the ease with which the system can be forced into a ferromagnetic state by the application of a magnetic field, the transport properties in zero field and appearance of a field – induced conducting state.

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